

Letters to the Editor

I wish to correct an error which appeared in my review article entitled: "Potential Dilemma: The Method of Meeting Automotive Exhaust Emission Standards of the Clean Air Act of 1970", EHP Vol. 8: 165-190, 1974. On page 177, I stated that BaP concentration in the exhaust emissions was a function of the lead deposits on the engine cylinder wall. The implication being that BaP concentration in exhaust emission was a function of gasoline lead content. These conclusions were drawn from the work of G. P. Gross. (The effect of fuel and vehicle variables on polynuclear aromatic hydrocarbon and phenol emissions. Paper No. 720210 presented at SAE Automotive Engineering Congress, Detroit, Michigan, January 10-14, 1972).

In a subsequent report, (CRC-APRAC Project No. CAPE-6-68. Fourth Annual (Final) Report on Gasoline Composition and Vehicle Exhaust Gas Polynuclear Aromatic Content, October 31, 1973) this error was rectified. Lead and phosphorus deposits on cylinder walls did not appear to influence BaP concentrations in exhaust emissions. The major variable affecting BaP concentration in exhaust emission was the fuel content of BaP. BaP concentration in exhaust emissions was also strongly influenced by the rate of oil consumption during engine operation.

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I enjoyed reading the paper "Potential Dilemma: The Methods of Meeting Auto-

motive Exhaust Emission Standards of the Clean Air Act of 1970" by Warren T. Piver in the August issue of *Environmental Health Perspectives*. I was particularly interested in the several pages on methylcyclopentadienyl manganese tricarbonyl, which my company now markets as an octane improver for unleaded gasoline under the name "Ethyl" MMT. There are a few inaccuracies in the discussion of MMT, and I thought it would serve a useful purpose to bring them to your attention.

Our recommended maximum use concentration of MMT in gasoline is 0.125 gram of contained manganese per gallon, which corresponds to 0.5 g/gal of the compound. The antiknock data at 0.25 g Mn/gal in the *Automotive Engineering* article cited in your paper were obtained to help us determine what our maximum recommended concentration should be. The 0.125 g/gal was based on considerations of engine durability problems at higher concentrations and on less attractive octane economics at higher concentrations, since the incremental effectiveness of antiknocks tends to level off at higher concentrations. (Incidentally, the *Automotive Engineering* article does not, as your paper states, say that 0.25 g Mn/gal has the same octane boosting and antiknock characteristics as TEL. Nowhere does it make any comparison with TEL.)

The recommended upper limit of manganese concentration is pertinent both to the treat cost and to the expected airborne manganese concentrations due to use of the product. The treat cost would be much lower than the 2.5-4¢/gal estimated in your paper. At our current price of \$2.55/lb of MMT the maximum treat cost would be $255¢/\text{lb cpd} \times 1 \text{ lb}/454 \text{ g} \times 0.5 \text{ g cpd}/\text{gal} = 0.28¢/\text{gal}$.

On expected airborne concentrations, you project a use level of manganese about 1/6 that of present lead levels, and, based on 1968 EPA Air Quality data, conclude that the increase in airborne manganese, if all gasoline contained it, would be $0.35 \mu\text{g}/\text{m}^3$. Actually, the relative use concentrations of manganese to lead would be about 1/20— $0.125 \text{ g Mn}/\text{gal}$ maximum versus a national pool lead content of about $2.5 \text{ g}/\text{gal}$ in 1968. In the 1969 National Air Sampling Network survey, the median airborne lead concentration, based on quarterly composite samples, was $1.0 \mu\text{g}/\text{m}^3$, rather than the $2.0 \mu\text{g}/\text{m}^3$ used in your paper. The expected median urban Mn concentration due to MMT would be one-twentieth of this, or $0.05 \mu\text{g}/\text{m}^3$.

In your paper there is considerable speculation as to the nature of the exhaust products to be expected from combustion of MMT. This is an area in which we have done a good deal of work, which is summarized by Ter Haar et al. in their paper "Methylcyclopentadienyl Manganese Tricarbonyl as an Anti-knock: Composition and Fate of Manganese Exhaust Products", presented at the APCA 67th Annual Meeting in Denver, Colo., June 1974. First of all it is correct, as you suggest, that no scavenger is used with our manganese additive. We have identified the manganese exhaust product as Mn_3O_4 . We have found that only traces of unburned MMT are exhausted, less than 0.5% of the manganese burned, usually less than 0.1%. We have found that the more efficient the emission control device on the car, the smaller amount of unburned MMT exhausted. In prototype 1975 lean reactor cars, it corresponds to 0.01–0.02% of the total manganese burned.

This trace of unburned MMT emitted decomposes rapidly in sunlight through light-catalyzed oxidation. We have extensively studied the products of its photolytic decomposition, and find that almost all the manganese is converted to manganese oxides and carbonates. The organic portion appears to be a complex mixture of acids, esters and polymers. We took particular pains to search for the presence of $\text{Mn}_2(\text{CO})_{10}$ or other

manganese carbonyl compounds, and were unable to find any.

On CO emissions from use of MMT, it can readily be calculated that in a car emitting CO in accordance with the 1975 standards ($15 \text{ g}/\text{mile}$), addition of MMT at our maximum proposed concentration would add 0.13% to this amount, so that the resulting CO emissions would be $15.02 \text{ g}/\text{mile}$, assuming that all the CO in the molecule is emitted as CO rather than being oxidized to CO_2 , a most unlikely situation. (This calculation assumes 10 miles per gallon of gasoline.)

You speculate that MMT exhaust products could participate in the formation of polycyclic aromatic exhaust particulates. In point of fact, we have found that use of MMT can reduce BaP emissions very substantially.

You cite Sullivan, who in turn refers to Bracewell and Gall, to postulate a possible effect of MMT exhaust products on atmospheric sulfate levels. Our work, summarized in Wright et al., "The Effect of Manganese on the Oxidation of SO_2 in the Air", also presented at the APCA 67th Annual Meeting, does not support such a prediction. In simulated atmosphere work at room temperature (as opposed to the Bracewell et al. work in solution) we found that manganese has no effect on SO_2 oxidation below about 70% relative humidity, and that even at 90% relative humidity and above, there is essentially no effect at concentrations of manganese below about $30 \mu\text{g}/\text{m}^3$, much greater than to be expected from use of MMT.

In the Wright et al. work a small amount of car exhaust containing the combustion products of MMT was used as a source of manganese. This manganese is in the form of Mn_3O_4 , as determined by x-ray diffraction. The manganese particles were very small, nearly all of them less than $0.2 \mu\text{m}$ mass media diameter, as determined by Andersen impactor measurements.

Our data suggest that the oxidation of SO_2 under high humidity conditions is controlled by the aqueous layer which surrounds atmos-

pheric particulates. At high relative humidities, greater than 75%, a great deal of water condenses on the particulate present in the atmosphere. The SO_2 dissolves in this aqueous layer. By adding ammonia to this system the pH is raised. There is a great deal of literature which shows that SO_2 is oxidized much faster in solution at a higher pH. It, therefore, appears that the rate of SO_2 oxidation under these conditions depends on the amount of condensed water and its pH.

The uncatalyzed oxidation of SO_2 to SO_3 does not occur in the dark. The photochemical reaction rate in clean air is slow, about 0.1% per hour. The presence of hydrocarbons and NO_x speeds the reaction. McKay has calculated that as little as 5 μg of ammonia per cubic meter under conditions of high humidity would cause the oxidation to proceed at 15%/hr. At low humidity, the reaction is much slower because of the reduced volume for SO_2 solution present on the surface of the particulate. Compared to these rates of reaction, the presence of 4 μg Mn/m^3 has no measurable effect on the reaction rate.

Moreover, there are several aspects of the way Bracewell and Gall express their results that create the impression that sulfate concentrations in the air could be very high due to these oxidative processes. Actually, the rate of conversion they report is only 1.4%/hr, based on their starting concentration of 1750 μg SO_2/m^3 and their predicted formation of 25 μg of sulfuric acid m^3/hr . Further, their SO_2 concentration of 1750 $\mu\text{g}/\text{m}^3$ is about 5–10 times typical airborne concentrations. The U.S. Department of Health, Education and Welfare has published a report entitled "Air Quality Criteria for Sulfur Oxides" (Jan. 1969). This report shows that for eight large cities only Chicago averaged more than 300 μg SO_2/m^3 . Most others averaged less than 200 μg SO_2/m^3 . If the rates of Bracewell and Gall are correct, the production rate of sulfate at more typical SO_2 concentrations would be about 2.5 to 5 $\mu\text{g}/\text{hr}$. Further, the rates reported by Bracewell and Gall are initial reaction rates. They found that the rate slowed markedly soon after the

reaction started, so that after about 10 min it was much slower. On another point, after examining the data of these authors, we do not understand their conclusion that 3 μg Fe/m^3 will oxidize SO_2 more slowly than 0.2 μg Mn/m^3 . Their Figure 4 shows iron to be equal to manganese in its ability to oxidize SO_2 .

Three other groups—Matteson et al., "Kinetics of the Oxidation of Sulfur Dioxide by Aerosols of Manganese Sulfate," *Ind. Eng. Chem. Fundamentals*, 8, 677–87 (1969), Johnstone, et al., "Absorption of Sulfur Dioxide from Air," *Ind. Eng. Chem.* 8, 1169–72 (1958), and Cheng et al., "Contribution to the Reaction Kinetics of Water Soluble Aerosols and SO_2 in Air at PPM Concentrations," *Atmos. Environ.*, 5, 987–1008 (1971)—have investigated atmospheric reaction of SO_2 and manganese. They used very high levels of manganese, and extrapolation of their results to 0.2 μg Mn/m^3 (the concentration used by Bracewell and Gall, but still higher than expected ambient concentrations) gives rates about 500 times slower than that of Bracewell and Gall.

You speculate that use of MMT could create a health problem to the general public because of the increase in popularity of self-service gasoline stations. We believe that such risk would be negligible. MMT has no greater level of chronic toxicity than does TEL (TLV is 0.1 mg/m^3 for TEL and 0.2 mg/m^3 for MMT). The volatility of MMT is much lower than that of TEL (0.052 mm Hg at 70°F for MMT and 0.30 mm Hg at 70°F for TEL). As brought out above, the concentration of MMT will be much less than has been the case for TEL. Specifically, 2.5 g Pb/gal is equivalent to 0.012 mole of TEL/gal and 0.125 g Mn/gal to 0.0023 mole MMT/gal. Taking the average gasoline molecular weight to be 105 and the specific gravity to be 0.735, and assuming ideality of both solutions, we can calculate that the partial pressure of MMT in gasoline at 70°F would be approximately one-thirtieth that of TEL, ignoring the rapid degradation of airborne MMT by light-catalyzed oxidation

which would reduce the MMT partial pressure to an even smaller value.

It is obvious from the above that the possibility of hazardous exposure of customers has to be much lower even than would be the case for TEL. When this is considered in light of the studies of Kehoe et al. in the 1960s on lead alkyls and service station attendants (who would have more exposure than self-service customers) in which it is concluded that no hazard existed, it would be extremely difficult to visualize the possibility of any hazard from use of MMT.

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Dear Sir:

We noted in a recent publication by Hinners et al. (1) that they had taken care to evaluate potential interferences in their atomic absorption spectrophotometric analyses of hair for sodium, magnesium, potassium, calcium, manganese, iron, nickel, copper, zinc, cadmium and lead. We were initially pleased to note that *full recoveries indicated no interferences* since we had earlier reported that there were no interferences when atomic absorption was used to determine cadmium, copper, lead and zinc (2). However, we did find the use of the expression *full recoveries* unusual since the percent recovery for each metal is usually reported and should have been included in this publication. On reading further we were disappointed to find a poor sense of logic in their discussion of interferences.

These authors had suggested that: *since additions of standards to portions of both their extracts and digests gave full recoveries indicating no interferences, calibration by the method of standard additions was not necessary*. What is confusing here is that

additions of standards to portions of the extracts and digests is calibration by the method of standard additions. This error in logic is compounded by their statement that: *the use of the method of standard additions seems redundant after demonstrating that interference was absent*, since they had apparently used the method of standard additions to obtain the results which indicated a lack of interferences. We presume that the end of their above statement should have been more correctly written as: *interferences were absent*.

We also wish to point out that additions of standards to digests can not be used to claim total recovery since this technique does not evaluate losses, if any, in the process of digestion. It would have been better to have added the standards to the hair samples prior to digestion.

It does seem redundant that these authors after having correctly done recovery studies first, which suggested that their analyses for all metals determined were interference free, evaluated the presence of negative ionization and chemical interferences which if present would have been inconsistent with full recoveries. Another possible interference which appears to be absent, with assumed recoveries of the order of 100%, but was not mentioned was a matrix-matching interference. With full recovery of each metal while using a background corrector the data were in hand to claim the absence of all of these interferences.

It would have been simpler to first do recovery studies by the methods of interpolation and additions, using the data routinely obtained in the usual operation of the atomic absorption spectrophotometer in the method of additions, with the use of a background corrector to eliminate absorption interferences. If total recoveries of the order of 100% were obtained, there would be no need to evaluate chemical, ionization or matrix-matching interferences. In this case the method of interpolation, which is usually more convenient to use, could have been